

“On the Method of Condensation in Calorimetry.” By J. JOLY, B.E., Assistant to the Professor of Civil Engineering, Trinity College, Dublin. Communicated by Professor FITZGERALD, F.R.S. Received June 28. Read November 18, 1886.

[PLATES 6 and 7.]

Introduction.

This paper is devoted generally to experimental verification of a method of condensation applied to the determination of specific heat. The extension of the method to the calorimetry of latent heat of gasification has been the subject of some experiments, but the further delay necessary to complete these compels me to defer their consideration. Similarly its application, theoretically practicable, to the direct determination of the specific heats of gases at constant volume, is not here considered.

In another paper (p. 250) some results bearing on the possible value of the method in physical mineralogy and in determinative mineralogy are given. The method was originally devised in the hope that it might be of service in this branch of investigation.

On the subject of this paper a couple of brief notices only have up to the present been published. One of these arose out of an informal notice brought before the Royal Dublin Society;* the second from a verbal account laid before the Dublin University Experimental Science Association.†

To the facilities extended to me by Prof. Fitzgerald, in the Physical Laboratory of Trinity College, the whole of the experimental verification of the method is due. I have not attempted to acknowledge anywhere adequately how much is due to his advice and suggestions.

Theory of the Method.

If W grams of a substance at the temperature t_1° of its surroundings be immersed in an atmosphere of saturated vapour, steam suppose, the temperature of which at the prevailing atmospheric pressure is t_2° , the substance experiences a rise in temperature of $t_2^\circ - t_1^\circ$, and absorbs a number of calories, $WS(t_2^\circ - t_1^\circ)$, where S is the specific heat of the body. Also if λ is the latent heat of steam at the temperature t_2° , a quantity of steam weighing w grams is condensed, so that

$$WS(t_2^\circ - t_1^\circ) = w\lambda.$$

If in this equation λ be known, the value of S may be found by

* ‘Irish Times,’ February 17, 1885.

† ‘Dublin University Review,’ June, 1885.

observation of the remaining quantities. The value of λ has been accurately determined by Regnault and recorded for all values of t_2° likely to occur. By similar observations, knowing S , λ may be the unknown quantity sought for by experiment, and determined from the equation. A substance of known specific heat being in this case immersed in a vapour of unknown latent heat.

It is evident that of the quantities to be measured the measurement of the value of w alone presents any difficulty. I have found, however, that w is accurately determined by weighing the quantity of vapour condensing on the surface of the substance in its transition of temperature from t_1° to t_2° ; and the calorimeters described in this paper are in short contrivances permitting the accurate determination of the weight of condensation as it gathers and falls from the surface of a substance suddenly surrounded by an atmosphere of steam. As the process is one principally of weighing, I have called the apparatus a *gravimetric calorimeter*.

Up to the present I have only employed the condensation of water-vapour in effecting determinations of specific heat gravimetrically. There are evidently sufficient reasons in favour of its use, chief among these is the accurate knowledge we possess of its latent heat through Regnault's experiments. But the ease with which it may be generated, and its chemical inertness when in presence of the materials of the calorimeter, are also important. The range of temperature too involved is sufficiently considerable, and, for my purpose, allowed of convenient comparison with the data of Regnault and others on specific heat obtained generally through this same range. By the use of other vapours greater weights of condensation are obtainable, but this is only of consequence when dealing with very small quantities of matter. The variations, however, in the upper limit of temperature thus obtainable might be otherwise important.

Description of a Gravimetric Calorimeter.

Whatever vapour be used in this method of calorimetry, two chief conditions must be attended to in its employment: (1) sudden replacement of the air surrounding the substance by the vapour to be condensed; (2) perfect mechanical conditions permitting the evaluation of the weight condensed while the substance is still surrounded with the vapour.

To effect the first of these conditions we might evidently either introduce the substance quickly into a chamber filled with and supplied with the vapour, or, maintaining the substance throughout in one chamber, replace the air around it by sudden and rapid inflow of the vapour. In choosing the last we dispense both with much contrivance and manipulation involved in the first. The error of trans-

ference obtaining in all other methods is almost entirely avoided, and in fact the facilities offered by the method are more fully availed of. We have in fact a change of state method which involves, as I hope to show, no sensible radiation errors, the simplest thermometry and apparatus, and no manipulative difficulties whatsoever.

Plate 6 is from a photograph of the apparatus. The calorimeter consists of a nearly spherical chamber of very thin spun brass, 10.5 cm. in diameter, made up of two hemispheres meeting on thin ground flanges. These hemispheres are carried by standards which slide upon the centre one of three rails forming a light girder. This girder is supported on three feet, and is arranged to stand in one assigned position inside the case of a large physical balance. I used it for a considerable time exactly in the position of the bridge used for supporting a beaker in taking specific gravities; that is, spanning one of the pans and passing between its stirrups. I subsequently found it necessary to remove the pan, substituting a counterpoise. It will be understood now that when the standards carrying the hemispheres are slid along the centre rail, the sphere can be completed inside the balance case, and when meeting about the centre of the rail, may be made to enclose a substance depending from the hook of the balance. To permit of the substance being weighed while thus enclosed in the sphere, a notch is provided in the flanges at their top meeting point. This notch is, for reasons to be explained later, cut in two little plugs of plaster of Paris, contained in cells provided for them. The sphere has two openings with short tubulures, one on each hemisphere, horizontal, and opposite one another. The larger of the two, 2.2 cm. diameter, opening to the front of the balance, serves for the admission of steam; the other, which when in use is prolonged by the addition of a couple of centimetres of rubber tubing, is about 1 cm. in diameter, and serves for the exit of steam at the rear of the balance.

To secure the more sudden admission of steam, a movable admission pipe fitting the front nozzle on a ground joint is provided. It is carried on a separate standard, also fitting the centre rail, and is connected with a small tin or copper boiler* by a flexible tube, so that when it and the rubber tube connexion have been first thoroughly heated by the passage of steam, it can be run up on the centre rail to meet the nozzle and discharge the steam directly into the sphere. Over the entire length of the calorimeter extends a rectangular tunnel-shaped covering of mahogany, made in halves, meeting at the centre of the girder, and provided with notches at their meeting faces, also cut in plaster of Paris, to permit the passage of the wire sup-

* I use a cylindrical copper boiler, 15 cm. diameter by 20 cm. high. This, heated by a strong Bunsen burner, evolves steam at the rate, I find, of about 0.4 gram per second. As it is important to introduce the steam as quickly as possible, a large boiler is advantageous.

porting the substance contained within the sphere. But one-half this covering is shown in the plate. It is borne upon the two outside rails of the girder, which between the rails is filled in with mahogany. The tunnel serves to isolate the calorimeter completely from the mechanism of the balance, and thus arranged I can detect no errors due to escape of heat. The apparatus might, however, also be arranged to stand beneath the balance, the balance being supported on a shelf, and a wire carried down from it to the calorimeter.

The little screws seen at the feet of the standards bear against the upper surface of the rail, enabling the standards to be adjusted for the accurate meeting of the ground joints. This is effected once for all. For smooth working the standards are clipped sideways against the rail by spring straps. Thumbscrews on top of the standards permit axial motion of the several parts, enabling the hemispheres to be adjusted for the free passage of the wire. The steamways are insulated from the standards by split rings of hard wood. Beneath the sphere, and accommodated by a gap in the central rail, a little vessel is placed for catching the water which drips from the sphere during experiment. The correct position of the girder is secured by means of a plate fixed to the floor of the balance, and provided with recesses to receive the feet of the girder. The girder is thus placed in position, and may be lifted in and out as required, without necessity of any readjustment.

The support for carrying the substance being experimented on, and the bucket for catching the condensed vapour dropping from it, are shown about full size in Plate 6. It is best to have these made of platinum. The conical bucket shown to one side of the carrier, and which, when in use, rests on the little claw beneath the latter, is of thin platinum foil. The rest is of platinum wire. This design secures slighthness and strength—over 100 grams may be placed on the cross wires—and supports the substance so that it is freely exposed to the steam on all sides, while the bucket beneath can be conveniently removed for cleaning and drying. Buckets made of silver foil quickly tarnish, owing to impurities in the steam. They prove less constant in calorific capacity than those of platinum.*

Method of Making an Experiment.

In exemplification of the manipulation involved in making an experiment, I describe one made on cast zinc. The piece of zinc is probably nearly pure. It weighs 48·300 grams.

About an hour before we make the experiment it is placed on the carrier, which depends by a fine platinum wire from the hook of the

* All the apparatus described in this paper is the workmanship of Yeates, of Dublin, and leaves nothing to be desired.

balance. The hemispheres of the calorimeter are then run up on the rail from each side of the balance and closed around the carrier. They are placed so that the wire passes freely through the aperture provided. A thermometer graduated to the tenth part of a degree Centigrade is next inserted in the tubulure opening to the front of the balance, so that its bulb projects well into the sphere. The tunnel-shaped covering is placed in position, and the piece of zinc and the carrier counterpoised. The balance is sensitive to half milligrams.

We assume that the thermometer indicates closely the temperature of the zinc after the lapse of about an hour. At the end of that time the boiler is heated up, and steam passed briskly through the leading tube to heat it throughout. This tube is of a length permitting the boiler to be placed at a safe distance from the calorimeter. The thermometer, where it projects from the sphere, is now read, in doing which it is necessary to remove the front half of the tunnel for a moment. The temperature indicated is $10\cdot73^{\circ}$ (corrected at Kew), the last number by estimation.

The thermometer is now withdrawn and the admission pipe slid quickly along the rail up to the calorimeter, the leading tube being pinched for a moment during this brief operation. Steam is now flowing rapidly into the calorimeter; in a few seconds it begins to escape at the exit tube to the far side of the balance. When it is seen to come out freely a valve on the boiler is opened, and so much steam diverted directly into the air that it now issues but slowly from the exit tube of the calorimeter.

The balance being let down on its bearings, weights are added till equilibrium obtains. If the substance is quite heated this weight remains absolutely adequate, if not the weight is again adjusted when no further increase is apparent. After the space of about one minute we find the balance continues to vibrate equably; we observe it for some five or ten minutes, and see that there is no change in the equable vibrations of the pointer. We are sure then that the total weight of condensation is obtained. It is found to be $0\cdot798$ gram.

A thermometer—also reading to tenths—inserted in a little tubulure provided for it on the boiler, reads $100\cdot25^{\circ}$ (corrected at Kew).

The experiment is now completed, and it only remains to make a couple of corrections on the value obtained as the weight of condensed steam before calculating the specific heat of the piece of zinc. Two corrections are necessary—

(1.) The bucket has, by a previous experiment, been found to condense $0\cdot031$ gram of water over a range of $87\cdot90^{\circ}$. The range in our experiment is $100\cdot25^{\circ} - 10\cdot73^{\circ} = 89\cdot52$. Therefore the deduction for the bucket is—

$$0\cdot031 + \frac{89\cdot52 - 87\cdot90}{87\cdot90} \times 0\cdot031,$$

or $0\cdot0315$ very nearly.

(2.) The piece of zinc was counterpoised in air, but the density of steam being less than that of air there was an apparent increase of weight on the replacement of the air by steam, to an amount equivalent to the volume of the substance multiplied by the specific gravity of steam (air being unity) at the pressure prevailing. It is sufficient to take this generally as equal to 0·00062 gram per cubic centimetre displacement (see Appendix). Taking the specific gravity of zinc as 7, and its weight being 48·300 grams, the value of the correction is—

$$\frac{48\cdot3}{7} \times 0\cdot00062 = 0\cdot0043 \text{ gram.}$$

The total deduction from the weight of condensation observed is then 0·0358; we take this as 0·036 in view of the limits of accuracy imposed by the balance. This leaves, as very nearly the true condensation due to the calorific capacity of the piece of zinc raised from t_1 to t_2 , the weight 0·762 gram. The quantities are now collected—

$$W = 48\cdot300$$

$$w = 0\cdot762$$

$$t_1 = 10\cdot73^\circ$$

$$t_2 = 100\cdot25^\circ$$

$$\lambda = 536\cdot4, \quad \text{at this temperature (see Appendix).}$$

Then by the formula previously given

$$S = \frac{w\lambda}{(t_2 - t_1)W}.$$

$$\begin{aligned} \text{Specific heat of zinc} &= \frac{0\cdot762 \times 536\cdot4}{(100\cdot25 - 10\cdot73) \times 48\cdot3} \\ &= 0\cdot09453. \end{aligned}$$

Degree of Accuracy attained by the Method.

In a similar way the quantities recorded in the following tables of experiments on metallic elements have been obtained.

Table of Experiments on some Metallic Elements.

Zinc.—Cast and cooled slowly. Free from arsenic, and probably nearly pure.

W.	t_1 .	t_2 .	w.	Sp. h.	Other observers.
48·300	15·70	99·76	0·714	0·09434	Bède 0·09412
„	15·74	99·80	0·713	0·09421	10° to 100°
„	15·86	99·80	0·713	0·09434	Bunsen 0·0935
„	10·73	100·25	0·762	0·09453	Regnault 0·09555
„	13·80	100·20	0·7345	0·09443	Kopp 0·0932
..	..	..	..	..	Dulong and Petit 0·093
Mean	14°	100°	..	0·09437	

Aluminium.—Pure, cast.*

W.	t_1 .	t_2 .	w .	Sp. h.	Other observers.
5·376	16·62	100·18	0·1880	0·2247	Mallet 0·225
„	16·30	100·18	0·1862	0·2215	Regnault 0·2181
„	15·78	100·18	0·1897	0·2242	Kopp..... 0·202
„	16·16	100·18	0·1887	0·2243	
„	16·42	100·18	0·1877	0·2236	
„ ..	16·42	100·18	0·1877	0·2236	
Mean	16°	100°	..	0·2236	

Silver.—Pure, rolled.*

W.	t_1 .	t_2 .	w .	Sp. h.	Other observers.
4·027	12·96	99·74	0·0380	0·0583	Regnault 0·05701
„	10·72	99·35	0·0380	0·0571	Kopp 0·056
„	11·44	99·28	0·0375	0·0559	Bunsen 0·0559
Mean	12°	99°	..	0·0574	

Platinum.—Rolled. Purity uncertain.

W.	t_1 .	t_2 .	w .	Sp. h.	Other observers.
34·764	13·10	99·63	0·182	0·0326	Regnault..... 0·0324
„	13·20	99·63	0·183	0·0327	Kopp 0·0325
„	14·36	99·52	0·186	0·0331	Pouillet 0·0335
„	14·04	99·54	0·183	0·0330	0° to 100°.
„	13·68	99·60	0·183	0·0328	
„	12·80	99·75	0·185	0·0328	
„	14·16	99·82	0·182	0·0328	
Mean....	14°	100°	..	0·0328	

Lead.—Pure, cast.

W.	t_1 .	t_2 .	w .	Sp. h.	Other observers.
89·503	16·70	99·85	0·428	0·03091	Regnault..... 0·0307
„	16·34	100·04	0·431	0·03093	„ 0·0314
..	..	..	..	..	Kopp 0·0315
Mean....	16°	100°	..	0·03092	

* Received from Professor Reynolds.

Some diversity of result exists among the determinations by other experimenters. Probably much of this diversity is to be ascribed to actual difference in the molecular condition of the samples operated on. The veracity of the present method must be judged then by general agreement with previous observations. In the case of *zinc*, however, the most reliable observations are probably those of Bède, Bunsen, and Regnault. The first of these observers, it will be remembered, extended his observations to the variations in the specific heat of zinc with change of temperature limit.* From those observations the value for the mean calorific capacity between 10° and 100° is deduced as 0.09412. This is identical, it may be said, with the value found by the method of condensation.

Compare, also, in this list of experiments on zinc—and throughout the table—the variations of temperature interval, sufficiently revealed in the varying values of t_1° , with the delicate compensating variations in the weights of condensed vapour, resulting in the close agreement of the values deduced. It will be seen too that among the five results on zinc the extreme variation from the mean amounts to no more than 0.17 per cent.

The experiments on aluminium, silver, and platinum tax more severely the consistency of the experiments, owing to the limits of accuracy imposed by the balance. Of the experiments made on *aluminium*, one is not recorded owing to a doubt about the accuracy of the initial temperature coupled with an abnormal result. The mean finally arrived at agrees with Mallet's experiments† effected in Bunsen's ice calorimeter. This value accords better with Dulong and Petit's generalisation than the lower values of Regnault and Kopp.

In the experiments on *silver*, much care had to be taken in estimating the value of w . No bucket was used, the specimen being looped in a fine platinum wire, the small quantity of water precipitated adhering to its surface. It is the smallest condensation I have attempted to deal with.

The series on *platinum* were some of the earliest effected by the method, and that in a very rude form of the apparatus. Two of the first experiments are not included in the list.

As, I think, some import may fairly be attached to consistency in experiments where prevailing conditions vary, I quote for comparison the extremes of Regnault's experiments on metals I have dealt with.

<i>Platinum</i>	569 grams	7 experiments..	0.03223—0.03279
<i>Zinc</i>	247 „	3 „ ..	0.09528—0.09589
<i>Silver</i>	345 „	5 „ ..	0.05679—0.05739
<i>Lead</i>	526 „	3 „ ..	0.03129—0.03150

* 'Mém. Couronnés de l'Acad. de Bruxelles,' vol. 27, 1856.

† 'Chemical News,' vol. 46, 1882, p. 178.

If these be compared with the extremes contained in the table it will be found that, except in the case of silver, the comparison is favourable to the method of condensation.

At the suggestion of Professor Fitzgerald, experiments on distilled water sealed in glass envelopes were undertaken. It appeared probable that the specific heat of this substance, as obtained in experiments made on a very large scale by Regnault, would afford more reliable data for comparison than metallic solids, in the case of which too it is likely that differences in molecular freedom may exist affecting the calorific capacity to a considerable extent. Again it was easy to obtain this substance sufficiently pure with facility. The experiments were carried out as follows:—

A very thin glass bulb is blown before the blowpipe. Its capacity is to be some 15 or 20 c.c. In drawing off the tube, a little hook is left for conveniently suspending the bulb in the calorimeter. It is sealed by closing the extremity of the hook; but before doing so we see that no appreciable quantity of moisture is enclosed, introduced from the breath in blowing it. If moisture is visible it is expelled by repeated heating and cooling, the cooling finally being effected several times in a desiccator. Neglect of this caused appreciable error in some of my experiments; it was ultimately detected in the abnormal specific heat ascribed to glass by the initial experiments on the envelope. It is probable that this trace of water, as suggested by Professor Fitzgerald, and contrary to my original idea when ignoring it, acts more by its latent heat of vaporisation than by its specific heat.

To ascertain the amount of precipitation to be allowed for this envelope, it is hung from a wire loop between the stirrups of the carrier, so that condensation falling from it is received in the bucket beneath.

The total condensation for bulb and carrier together with that due to the air contained in the bulb, including also the effect of displacement difference from air to steam, afford—

(1.)	$w_1=0.116.$		Range, 11.0—100.35°
(2.)	$w_1=0.116.$		Range, 11.3—100.35°

The bulb is now opened by removing the extremity of the glass hook, and weighed = 2.084 grams. The height of the barometer (760) and temperature (11°) are noted.

The next operation is to fill it with distilled water. This is effected under the receiver of the air-pump by exhausting while the orifice of the bulb is submerged, and again cautiously exposing to atmospheric pressure. A space is left unfilled to allow for subsequent expansion. The contents of the bulb are now raised to boiling point by immersing in a bath of boiling water, and it is sealed with the blowpipe while at this temperature. This is necessitated by the thinness of the

glass; it was found that such bulbs will not stand the internal pressure otherwise obtaining at steam temperature.

Its weight is now 15·930 grams. It is estimated that its content is altogether 16·5 c.c.; this quantity of air at 760 mm. and 11°, as above, weighs very closely 0·020 gram. The deduction for the weight of the glass envelope in order to deduce the weight of contained water is, then, 2·084—0·020 affording $W=13·866$.

In subsequent experiments with this bulb of water, it is necessary from the precipitation obtained to deduct w , as ascertained by experiments (1) and (2), above, diminished however by the quantity of precipitation to be ascribed to the calorific capacity of the contained air present in those experiments. Taking the specific heat of air as 0·2389, this retrenchment calculates to be nearly 1 mgrm. of precipitation, and it is taken as such as it probably contained still some moisture. This leaves the deduction as 0·115 for a range of 89·2°. Although the nearly constant displacement difference of the bulb from air to steam is here included, this quantity may without sensible error be recalculated for variations in temperature range as the correction on the large condensations subsequently obtained. The further process of experiment is the same as previously described in the case of zinc.

In this way, the six experiments contained in the following table have been carried out:—

Table of Experiments on Distilled Water.

No.	W.	t_1°	t_2°	λ .	w .	Sp. heat.
1	13·866	11·20	99·90	536·56	2·3125	1·0087
2	"	11·70	99·45	536·90	2·2760	1·0044
3	"	8·80	99·55	536·80	2·3610	1·0074
4	"	9·70	99·50	536·80	2·3320	1·0055
5	"	9·47	100·00	536·50	2·3530	1·0055
6	"	8·80	100·10	536·40	2·3740	1·0059
Mean ..		10°	100°	..	..	1·0062
Between same limits, according to Regnault, specific heat = 1·0055.						

The last four experiments in the table were carried out in such a way that the rate of precipitation was much retarded, in fact the conditions were altered to those prevailing in the case of a very badly conducting body. This was effected by shielding the glass bulb from direct contact with the steam by a loose fitting copper-foil box, an intervening air-jacket being left around the bulb. With this arrangement precipitation was hardly completed in 15 minutes; the naked

bulb was quite heated in something less than four. A deduction was of course made for the shield by preliminary experiments.

I would point out that any error in Regnault's estimate of the increase of specific heat of water with rise of temperature will militate in a double sense against the agreement of his results with mine. For this increase is assumed by Regnault in deducing, from his formula for the total heat of steam, the heat of evaporation, and, as it is subtractive, an error on the side of excess in his estimate of the specific heat of water introduces an error on the side of insufficiency in the value ascribed to λ , and *vice versa*. Thus not alone would the quantity with which I compare my results be erroneously assumed, but in proportion as error exists in its value, error in the opposite direction would be introduced into my results.

I add some experiments bearing on questions of radiation error as affected by extent and nature of surface exposed to the steam. They are from those made on minerals, and are embodied in a paper on the specific heats of minerals. ('Roy. Soc. Proc.,' vol. 41, p. 250.)

The following table contains cases where experiments were re-

Table I.

	W.	w.	t_1° .	t_2° .	Sp. heat.
Limpid crystal of <i>Barites</i> . . .	76·109	1·405	9·65	100·30	0·10923
A portion of the same in small fragments	65·143	1·195	9·60	99·80	0·10910
Rhombohedron of <i>Iceland spar</i>	33·904	1·156	10·00	99·76	0·20383
Same in small fragments	33·059	1·079	13·34	99·50	0·20345
Specimen of <i>Talc</i> in one piece..	47·445	1·685	12·32	100·25	0·21671
Two fragments from same hand-specimen	44·631	1·568	13·30	100·20	0·21686
Specimen of <i>Lepidolite</i> — one piece	42·726	1·470	12·20	100·20	0·20978
Two pieces from same hand-specimen	48·823	1·676	12·38	100·20	0·20967
Five crystals of <i>Amphibole</i> . . .	57·192	1·835	12·00	99·72	0·19634
The two largest of the five . . .	45·133	1·443	12·94	100·30	0·19635
The three largest of the five . . .	51·309	1·640	12·90	100·30	0·19619
Fragments of milk-white <i>Oligoclase</i>	48·074	1·546	12·60	99·10	0·19974
Pieces from same hand-specimen	41·829	1·366	11·60	99·40	0·19967
Flakes of <i>Biotite</i>	20·291	0·685	12·63	100·30	0·20651
Part of same	17·809	0·593	12·70	99·95	0·20491
Crystal of <i>Muscovite</i>	20·541	0·687	12·40	99·90	0·20519
Loose flakes from same hand-specimen	23·735	0·778	13·80	99·75	0·20466

peated under very different conditions of surface area. It is evident from them that the extent of surface exposed by a substance to the steam affects the result only in a very trifling degree; the repeated consistency can hardly be the result of chance. As liability to radiation errors will increase, *ceteris paribus*, with extent of surface, they reveal, I think, that the method is not open to appreciable error from such sources.

Table II illustrates, in the cases of gypsum, calcite, and aragonite, minerals fairly constant in chemical composition, fidelity to the chemical nature of a substance through varying conditions of weight, bulk, shape, and surface texture.

Table II.

	W.	w.	t_1° .	t_2° .	Sp. heat.
Hydrous calcium sulphate.					
<i>Gypsum</i> :—					
Clear crystal of selenite	21·048	0·965	10·00	100·10	0·27264
Four clear crystals of selenite	13·204	0·623	7·24	100·40	0·27164
Fibrous silky gypsum	30·150	1·393	9·20	100·40	0·27167
Fragments of rough white gypsum	} 31·547	1·456	9·98	100·40	0·27374
Calcium carbonate — <i>Calcite</i> , rhombohedral :—					
Iceland spar, limpid crystal..	33·904	1·156	10·00	99·76	0·20383
Milk-white rhombohedron ...	35·815	1·135	16·75	99·93	0·20439
Three slender hexagonal crystals, limpid	} 10·044	0·329	13·04	99·60	0·20340
Group of tapering, clouded prisms	} 31·524	1·075	11·90	99·50	0·20908*
White chalk, in fragments...	22·454	0·747	12·30	99·80	0·20415
White chalk, fragments from same specimen	} 21·737	0·706	13·77	99·35	0·20390
Calcium carbonate— <i>Aragonite</i> , orthorhombic :—					
Two yellow transparent crystals	} 24·331	0·806	12·45	99·65	0·20401
Two limpid crystals	28·161	0·934	11·60	99·00	0·20393

Apart from experiment, I think sufficiently careful consideration shows that we might expect very considerable accuracy from the method. There is theoretically, it will be found, but one source of error needing serious consideration; it is the danger of precipitation occurring, not on the surface of the substance, but at points close to

* For a brief notice of such abnormal cases see my paper "On the Specific Heats of Minerals," 'Roy. Soc. Proc.,' vol. 41, p. 250.

the surface; in other words, the formation of mist by radiation from the steam to the cold substance.

Now it is assured that on the replacement of air by steam a film of water is instantaneously deposited on the surface of the substance, and, assuming an abundant supply of steam, condensation then proceeds as fast as heat is transferred by conductivity and diffusion across this film to the cold surface of the solid beneath. While then we must assume that the inner surface of the film is appreciably at the temperature of this cold surface, it is probable that we may also assume the outer surface of the film to be throughout the experiment nearly at the temperature of the steam. There can be but little difference, for fall in temperature is made good with great rapidity by fresh condensation. There is here in the first place a favourable condition, as surface radiation can, under such circumstances, be but insignificant in amount, and radiation from points in the surrounding steam can only be supposed as affecting points within the film or, in some cases, within the substance. Only in this way can we suppose the formation of precipitation elsewhere than at the very surface of the film by actual contact. But again, the opacity of water to radiation from aqueous vapour will here afford protection. This opacity, it will be remembered, has been shown by Tyndall and others to be very great. Thus I find that Tyndall records among his experiments that a layer of water but 0.07 of an inch in thickness transmitted but 1.1 per cent. of the radiation from a hydrogen flame. It may be supposed that the more perfect accord between the vibration periods of radiator and absorber obtaining in the calorimeter will ensure greater, if not perfect, opacity.

The contact precipitation, consequent on the loss of *vis viva* of the impinging molecules—the film transmitting the energy to the substance—insures that there will be many molecules entering and few leaving, and hence extension of free path or diminution of pressure in directions normal to the surface of the substance. There is then super-added as a protective element a converging drift of steam upon the substance, tending to restore to it what precipitation may possibly be due to radiation. Under perfect conditions of steam supply—could we suppose, for example, the substance in a chamber which could be supplied with steam from so many points that we might substitute the idea of an unlimited region of steam suddenly brought around it—this drift, I think, excludes almost the possibility of error supposing radiation. In attainable conditions, where cross draughts will prevail to some extent, there would still evidently be protection involved in the very fact of condensation.

There are, then, three circumstances tending to nullify this error; the high temperature of the external surface, the adiathermanous nature of the water film, and the converging drift of steam. Whether

all three act, or whether the first two are not practically efficacious of themselves, I think that theory is here in accord with experiment in showing that on this count no appreciable inaccuracy is to be apprehended.

There are a few other considerations. From the facts that there is a fall of temperature across the film, the gradient descending nearly to the temperature of the substance on the one side, and that throughout the period of condensation the film continually gravitates downwards as it receives accretion from without, it might be expected that water which had not yet risen to steam temperature might in some cases reach the bucket. This occurs, but need obviously be no source of error. If experiments be made in glass calorimeters, the formation of a dew on the underside of the bucket will often be noticed; to this extent it does no harm. But in the case of sudden and copious precipitation, especially in the case of smooth substances, where water runs off more freely at points close to the surface of the body, the precipitation on the outside of the bucket may collect in such quantity that drops fall off. I have occasionally noticed this, and it should be borne in mind; but with the flat form of bucket used, and the safeguard afforded by the supporting claw, there is little danger of this occurring up to rapid precipitations not much exceeding a couple of grams. Over that amount a second catchwater, which may be of small dimensions, should be provided beneath the claw.

The substance hanging in the steam is safe from radiation errors. The phenomena attending accretion of weight terminate in the conditions which prevail in the case of a liquid in presence of a saturated atmosphere of its own vapour, the whole maintained at constant temperature and pressure, when the relative weights of liquid and vapour remain constant statistically, and absolutely so far as we can measure. If radiation from the hot substance to the cooler walls of the calorimeter occurred, constancy of weight would not be attained. It is certain that the least radiation across the steam-jacket would be revealed in continued slow accretion of weight. But there is nothing so striking in experiments effected by this method as the steadily maintained equilibrium of the balance once the substance has attained the temperature of the steam, the pointer vibrating with perfect equality so long, apparently, as we chose to prolong the experiment. If the steam supply be cut off for a moment there is loss of weight, and on restoration of steam there is finally on the whole gain of weight, for radiation, as well as evaporation, occurs in the absence of steam. If the pressure be appreciably increased by throttling the exit pipe and partially closing the boiler for a couple of seconds, the balance reveals increase of weight; but so long as the pressure is neither increased nor diminished equilibrium is absolutely preserved.

It is obvious that disturbing effect due to water-dust or mechanically

suspended water in the steam is negated by this constancy of weight. Probably such dust is all deposited in the steam pipe shortly after leaving the boiler.

Mist or water-dust doubtless is present at first, due to the condensation produced in heating up air in the calorimeter. Some of this is thrown upon the substance, but this will be small in quantity, probably inappreciable, and acts against what error is due to radiation from the incoming steam to the substance. This last is an error analogous to the error of transference in other methods, but with easily attainable rapidity of air displacement probably far less.

The degree of accuracy attainable in effecting the measurements remains to be considered. Of these, it is evident that in obtaining the temperature limits great accuracy is attained by the use of thermometers of no extraordinary sensitiveness. If t_1° and t_2° are reliable to $\frac{1}{10}$ part of a degree, over a range of 80° we are observing to $\frac{1}{800}$ part the quantity to be measured.

As regards the observation of w , the weight of water condensed, obviously the degree of accuracy attainable depends on the sensitiveness of the balance and the magnitude of w . It is also necessary, however, to consider in some detail how far it has been found possible to perfect the mechanical conditions attending the observation of the weight of the substance while immersed in steam.

It is evident in the first place that as regards the danger of introducing error into the equilibrium of the balance by heat radiating to its parts, the difficulty may at once be got over by arranging things so that the calorimeter is outside the balance case, as beneath it, the balance standing on a shelf, suppose, and a wire taken down through apertures in balance floor and shelf. In the form already described, indeed, I have detected no error due to unequal heating of the beam, although I have frequently looked for it by unhooking the substance during experiment and testing for want of equilibrium. This is due to the protection afforded by the non-conducting material of the tunnel. It was necessary, however, to retain but one pan, as heat conducted by the rails through the floor of the calorimeter set up a draught tending to draw up the pan.

I have detected no error, measurable by the balance, due to condensation on the wire for suspending the substance, where it issues from the calorimeter. If this wire be closely observed it will be seen that a little bead of water forms on it just above the mouth of the aperture, and although occasionally reinforced by another little bead slipping down to it, it soon reverts to its original bulk, probably by evaporation promoted by heat conducted along the wire. With the size of wire used—about 0.15 mm. in diameter—I do not think this bead of water ever exceeds half a milligram in weight, and, as I say, the balance shows no sign of any gradual increment of weight. This

experiment on the constancy of weight has been extended to over half an hour on many occasions.

The use of plaster of Paris in forming the aperture avoids what uncertainty and want of sensibility would be introduced into the weighing by water permitted to accumulate in the orifice. Until this plan of cutting the aperture in a bibulous material was resorted to, the accumulation of water gave much trouble. The plaster remains dry when in use for an indefinite time, and wears well. That now in the calorimeter has served through more than 300 experiments. It is also very easily renewed.

In order to avoid as far as possible escape of steam up the wire and ensure constancy of pressure, I have lately adopted a plan which acts automatically in keeping the calorimeter full of steam sensibly at atmospheric pressure. The arrangement consists in locating the escape valve of the boiler at a level so much below the level of admission into the calorimeter, that a small and constant pressure—due to the levity of the steam—is established, urging the gas to ascend the tube leading to the calorimeter. This end is secured by affixing the escape-valve to the end of a wide tube which is taken from the boiler bent twice at right angles and carried down to a level outside the boiler sufficient to secure the requisite pressure; a couple of decimetres “head” will in general be sufficient.

The effect on the weighing of steam draught within the calorimeter can be entirely avoided by shielding or jacketing. In the form already described, indeed, it seldom gave trouble, but in this respect I have in a recent form improved the apparatus. It is worthy of notice, also, that the conditions prevailing when we weigh a substance at a temperature different from that of the air within the balance case do not obtain here, the substance in the calorimeter being surrounded by an atmosphere at its own temperature.

Description of an Improved Gravimetric Calorimeter.

I have designed an apparatus intended to carry out such conditions as have suggested themselves as conducing to accuracy and to ready working. Its advantages have already to a great extent been practically tested in a recently completed instrument, but this instrument serving itself to suggest improvements is not the same as that now described. Plate 7 shows a vertical section and plan.

The apparatus it will be seen consists of a cylindrical chamber with conical ends. This chamber is divided in a vertical plane passing through its axis, the separate halves being firmly hinged on a tripod borne on three adjusting screws. The chamber is thus readily opened by turning back the halves, and closed by pressing them together, when they meet on a ground edge. It is made of brass and kept as

slight as possible. The half chambers being closed, steam is admitted at the top of the apparatus, the expelled air escaping at the bottom through a tube which passes through the base of the instrument. In plan it will be seen that the steam is admitted by a forked or branching tube at two tubulures, which in elevation are seen to be cut back so as to afford a ready seat for the supply pipe, and also that the latter when placed in position may conduce to bind closer the half-chambers. The steam pipe is supported further and retained in position on a light pillar springing from the tripod base. To its seat on this pillar it is clipped by a spring bearing against the centre of the fork, but so that it may readily be laid in its position. A little tubulure is also provided for conveniently taking the temperature by inserting a thermometer.* At other times this tubulure is closed by a little cap (not shown in the drawing). Two half-cylindrical plugs of plaster of Paris, notched at their meeting faces, serve as before to pass the wire depending from the balance, which is supposed to rest upon a shelf placed above the apparatus.

Within the outer shell of the calorimeter an inner shield of very slight brass is provided, similar in shape, and capable of a rotational motion of about 60° about its vertical axis. This is effected by attaching it to a tube which rotates smoothly in the exit-tube at the base of the calorimeter. It is worked by a stud projecting through a horizontal slot cut in the latter. The shield is made in halves, and opens on hinges affixed to the rotating tube. Above, each half of the shield is perforated, so that when in one extreme position it receives within it all the entering steam, but on being rotated 60° no longer admits steam directly, the perforations being then turned away from the entrance tubulures.

When it is desired to close the exit-tube of the calorimeter, a stop is pressed in through a horizontal slot in the tube. Water condensed from the steam by radiation from the calorimeter is received in a little trough placed beneath the tripod stand.

The apparatus is worked as follows:—

The carrier being suspended at the right height on the wire from the balance, and the substance being arranged upon it, the calorimeter, with its inner and outer cases drawn back, is moved under and then closed upon it. The inner case is now rotated so that the calorimeter is thus still further closed, and also one of the apertures of the shield, so placed that a thermometer may be passed through the small tubulure into the interior of the calorimeter. To guard the calorimeter against sudden changes of temperature while the thermometer is assuming

* The effect of scale parallax in reading thermometers may conveniently be avoided by bringing the scale into coincidence with its reflection on the mercury thread of the thermometer. The way of doing this is easily acquired after a couple of trials.

the temperature t_1° , it is necessary to provide a cover of nonconducting material—as wood—made in halves, and closing so as to permit the reading of the thermometer.

When it is desired to carry out the experiment, the forked tube, which is connected with the boiler by 2 or 3 metres of rubber tubing, is separately heated with steam, the valve on the boiler being closed. The thermometer in the calorimeter is then read and withdrawn, the cover removed, and the shield rotated into the position for admitting steam. The steam-pipe is now laid in position; the construction enables this to be done very rapidly and easily. Steam is thus passed directly into the inner chamber at two points, and the inner chamber being very slight condenses but a small quantity of steam, so that the displacement of the air is retarded as little as possible, and is, in fact, with the empty calorimeter almost immediate. On steam flowing out freely at the exit-tube, the valve in the boiler is opened and the calorimeter closed by pressing home the stop in the exit-tube.

The adjustment of the wire in the orifice is now effected by the screws on the tripod. Effected in this way this is a very easy operation, although the orifice may be hardly 1 mm. in diameter and the wire some 40 cm. long. Balance and calorimeter must, however, be steadily supported. The weighing is now begun, and when it is found that the substance is no longer condensing steam, is finished with the shield in the calorimeter in its position for sheltering the substance from draughts. On this operation being completed, the thermometer for taking t_2° is inserted in its tubulure, which is now again over one of the orifices in the inner shield and hence admits the thermometer freely into the calorimeter.

Appendix.

Corrections for Displacement in Steam.

(1.) The substance being counterpoised in air is not when immersed in steam—apart from the occurrence of condensation—any longer in equilibrium with the counterpoise, the density of saturated steam at ordinary pressures being different from that of air. The deduction from the apparent weight of condensation on the substance is equivalent to the volume of the substance multiplied by the difference in the weights of unit volumes of steam and air. By the apparent weight of condensation is meant that deduced on subtracting from the weight added to the counterpoise during an experiment the weight due to condensation on the carrier. Let this apparent weight be w_1 .

The difference in the weights of unit volumes of steam at 100° and air at 15° is 0.000636, calculated on the absolute densities of dry air and steam according to Regnault.

The correction on w_1 is then—

$$-V \times 0.000636 \text{ gram,}$$

where V is the volume of the substance in cubic centimetres.

(2.) If extreme accuracy be desired, it is necessary further to reduce the weight of condensation to vacuo. Calling w_2 the weight deduced after correction (1), the second correction is on w_2 , and is—

$$+w_2 \times 0.000589,$$

the factor 0.000589 being the absolute density of saturated steam at 100° (Regnault). It is assumed that we may for the purpose consider unit weight of water at 100° as equal to unit volume.

Finally the true weight of water w is very nearly—

$$w = (w_1 - V \times 0.000636) \times 1.000589.$$

Regarding the factor 0.000636 I may mention that a direct experiment made in the calorimeter afforded 0.00062 as the difference in weight of unit volume of steam at 100.2° and air at 17.7° and 766 mm. The experiment consisted in hanging a heated sphere of blown glass in the calorimeter—it having been previously counterpoised—and admitting steam before the sphere had cooled to steam temperature. When a sufficient time had elapsed to secure equilibrium of temperature the amount necessary to add to the counterpoise to restore balance was ascertained; this divided by the volume of the sphere afforded the relative density sought.* In the experiment the volume of the sphere was 38.7 c.c., the weight added 0.024 gram.

On the Value of λ .

If the value of λ be calculated from Regnault's formula for, say, the cases of a barometer at 720 and 780, the values 537.2 and 536.0 are obtained; at 760 it is 536.5. In careful experiment this variation must be considered. My practice has been to allow for it by the approximate assumption for ordinary variations of pressure that the correction on the value of λ for the standard pressure 760 mm. is—

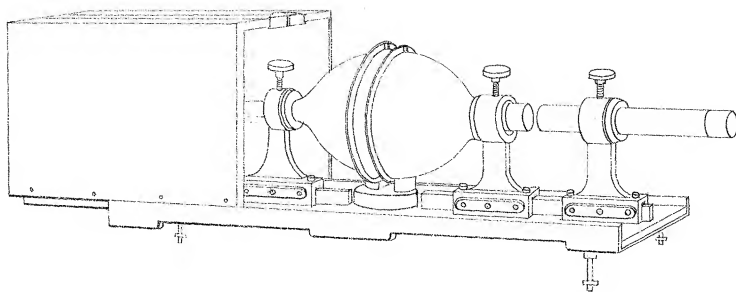
$$+0.7(100 - t_2^\circ),$$

that is I take

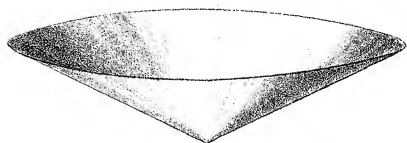
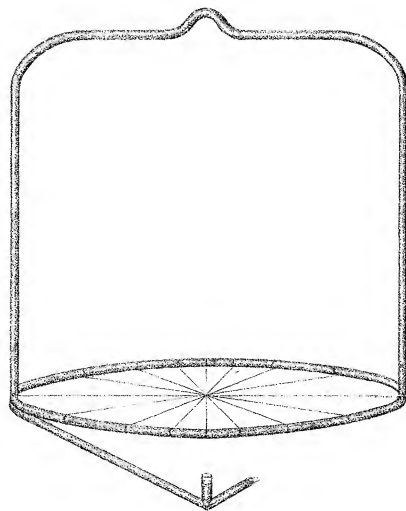
$$\lambda = 536.5 + 0.7(100 - t_2^\circ)$$

where t_2° is the temperature of the steam, read directly by a thermometer or deduced—as it conveniently may be and with great accuracy—from the height of the barometer and reference to Regnault's tables for the corresponding boiling temperature of water.

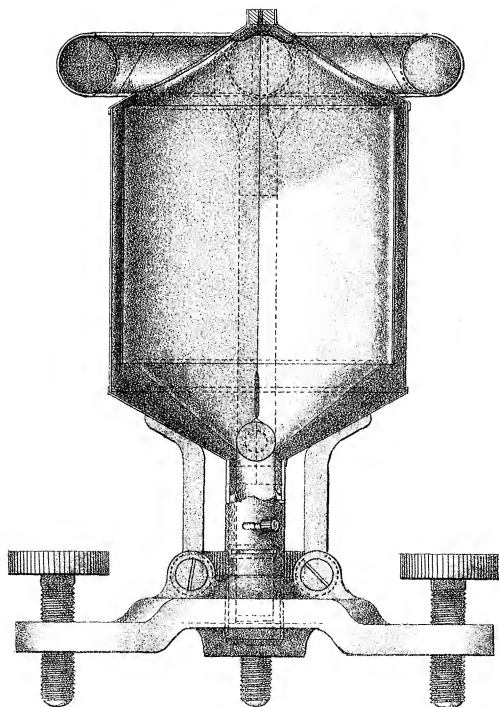
* See "On some methods of Measuring the Densities of Gases," by G. F. Fitzgerald, F.R.S., 'Roy. Dublin Soc. Proc.,' vol. 4, 1885, p. 481.



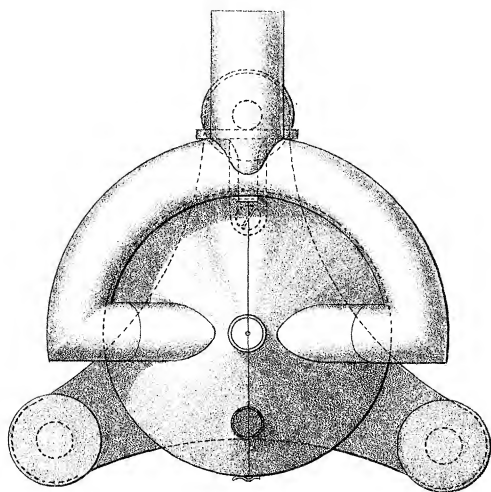
CARRIER AND PAN.



A GRAVIMETRIC CALORIMETER.



SECTIONAL ELEVATION.



PLAN.

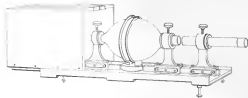
Complete Formula for Calculating the Specific Heat.

Collecting the foregoing corrections we get a formula for use if very considerable accuracy be desirable, but it is to be observed that under any ordinary circumstances correction (1) on w_1 of $-V \times 0.000063$ is sufficient.

The complete formula for S, the specific heat, is—

$$S = \frac{1.000589[w_1 - V \times 0.000636][536.5 + 0.7(100 - t_2^\circ)]}{W(t_2^\circ - t_1^\circ)},$$

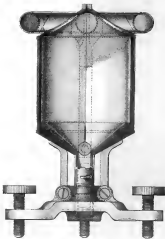
the several weights observed being supposed reduced to vacuo as usual, otherwise the letters being as before.



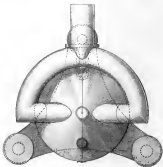
CARRIER AND PAN.



A GRAVIMETRIC CALORIMETER



SECTIONAL ELEVATION.



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